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(54) Method of Manufacturing a Fiber Reinforced Metal Matrix Composite

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Specification

1. Title of the Invention

Method for Manufacturing a Fiber Reinforced Metal Matrix Composite

2. Claims

A method for manufacturing a fiber reinforced metal matrix composite characterized in that it comprises:

a first step in which a bundle of continuous inorganic fibers is opened and the fibers are pulled and arranged in one direction, and they are thermal sprayed with matrix - metal to form a prepregnated sheet; and

a second step in which required pieces of said prepregnated sheets are laminated and set into a mold, and the mold is sealed into a metal foil bag under reduced pressure, and prepregnated sheets in said metal foil bag are subjected to liquid phase diffusion bonding.

3. Detailed Description of the Invention

(Field of Industrial Application)

The present invention relates to a fiber reinforced metal matrix composite (may be referred to as the "FRM" hereinafter) which is lightweight, highly strong, and excellently heat resistant, and is suitable for materials used in the areas of aerospace and automobile.

(Prior Art and Its Problem)

One of the methods for manufacturing an FRM includes a known manufacturing method in which inorganic fiber bundles are pulled and arranged, and they are thermal sprayed with matrix - metal by the use of plasma spraying to form prepregnated sheets, then, prepregnated sheets are laminated and bonded by liquid phase diffusion bonding.

However, in this method, if the metal matrix in use is active and the above-mentioned bonding is carried out in atmosphere, the surfaces of prepregnated sheets are oxidized and cannot be bonded well. For this reason, in the case in which prepregnated sheets are bonded with active metal in a matrix, heating and pressing must be carried out under a reduced pressure ambient or inactive gas ambient, necessitating the use of a press machine equipped with a vacuum chamber. Thus, FRM could not be manufactured economically and efficiently.

On the other hand, there is a simple method to solve the above-mentioned problem. In Mitsubishi Heavy Industries Technical Review, vol. 13, No. 3, p.p. 1 ~10, Hiroto Kawamura et al. describe a method in which a laminate of prepregnated sheets is inserted to a container made of a thin stainless steel plate having a thickness of 500 μm and subjected to liquid phase diffusion bonding under the vacuum vent condition ($1 \sim 5 \times 10^{-3}$ mmHg), thereby forming FRM.

Nonetheless, this method has a drawback. Since the container is made of the above-mentioned thin stainless steel plate, the container does not change its shape during vacuum-venting. And depending on the shape of the container or the insertion condition of the prepregnated sheet-laminate, unfilled space, which cannot be replaced with the prepregnated sheet-laminate, is left in the container in which prepregnated sheets are sealed under reduced pressure. And when the liquid phase diffusion bonding method is applied to the above-mentioned sealed container, discharging melted metal to the unfilled space makes it difficult to control the fiber volume ratio (V_f) and to maintain the shape of FRM constant.

(Means to Solve the Problem)

The present invention provides a method for manufacturing FRM which resolves the above-mentioned problem.

The present invention provides a method for manufacturing a fiber reinforced metal matrix composite characterized by comprising:

a first step in which a bundle of continuous inorganic fibers is opened and the fibers are pulled and arranged in one direction, and they are thermal sprayed with matrix - metal to form a prepregnated sheet; and

a second step in which required pieces of said prepregnated sheets are laminated and set in a mold, and the mold is sealed into a metal foil bag under reduced pressure, and prepregnated sheets in said metal foil bag are subjected to liquid phase diffusion bonding.

The fibers constituting a continuous inorganic fiber bundle may be, for example, silicon carbide fibers, silicon nitride fibers, boron nitride fibers, aluminum nitride fibers, silica fibers, boron type fibers, alumina type fibers, carbon type fibers, or Si - Ti type or Zr - C - O type inorganic fibers (Chirano Fiber® manufactured by Ube Industries, Ltd.) which are obtained by sintering polymetalloccarbosilane, wherein the fibers may be of a single type or a combination of these types.

Additionally, the inorganic fibers described by the present applicant in the claims in the specifications attached to the application (2) filed on August 11, 1990, as well as those described in the application (11) filed on September 1, 1989, are also suitably usable for the continuous inorganic fiber bundle of the present invention.

The inorganic fibers described in the specification attached to the above-mentioned application (2) are highly strong inorganic fibers with high elastic moduli characterized by being:

- (i) a carbonaceous material in at least one type of crystal arrangement state selected from the group consisting of a radial structure, onion structure, random structure, core radial structure, onion-skin structure, and mosaic structure derived from the mesophase polycyclic aromatic compounds constituting the polymer;
- (ii) crystalline and/or amorphous carbons in the non-orientation state derived from optical isotropic polycyclic aromatic compounds constituting the polymer including the component which is insoluble in the organic solvent; and
- (iii) an aggregate comprising an amorphous phase [substance] essentially comprising Si, C, and O and/or crystalline ultrafine particles essentially comprising β - SiC having a particle diameter of 500 Å or less, and amorphous SiO_x ($0 < x \leq 2$) wherein the Si - C - O substance comprises 30 ~ 70% by weight of Si, 20 ~ 60 % by weight of C, and 0.5 ~ 10 % by weight of O.

The fibers are obtained by the method for manufacturing fibers characterized by comprising the following [four] steps: In the first step, polycyclic aromatic polymers containing silicon are obtained by allowing i) and ii) below to undergo a reaction by heating and/or melting at a temperature within the range of 200 ~ 500°C where

- i) is 100 parts by weight of a random copolymer in which at least part of silicon atoms of an organosilicon polymer comprising mainly the bond unit (S - CH₂) or the bond unit (Si - CH₂), and the bond unit (Si - Si), wherein side chains of Si atom have a side chain radical selected from the

group consisting of a hydrogen atom, lower alkyl group, phenyl group, and silyl group, and the ratio of the total number of (Si - CH₂) bond units to the total number of (Si - Si) bond units is within the range of 1 : 0 ~ 20, are bonded to aromatic rings of petroleum - or coal pitch, or the compound resulting from its thermal treatment via the Si - C linking group; and
 ii) is 5 ~ 50000 parts by weight of a polycyclic aromatic compound in mesophase or dual phase of mesophase and optically isotropic phase obtained by thermal processing of petroleum - or coal - pitch.

In the second step, the spinning dope for the above-mentioned polycyclic aromatic polymer is prepared for spinning. In the third step, the spinning material yarn is made infusible under or in the absence of tension. And in the fourth step, said infusible spun fibers are sintered in vacuum or an inert gas ambience at a temperature within the range of 800 ~ 3000 °C.

Moreover, the inorganic fibers as described in the specification attached to said application (11) are highly strong inorganic fibers with high elastic moduli characterized by being:

- (a) a carbonaceous material in at least one crystal arrangement state selected from the group consisting of a radial structure, onion structure, random structure, core radial structure, onion-skin structure, and mosaic structure derived from the mesophase compounds constituting the polymer;
- (b) crystalline and/or amorphous carbons in the non-orientation state derived from optical isotropic polycyclic aromatic compounds constituting the polymer including the component which is insoluble in the organic solvent; and

- (c) ① amorphous phase [substance] essentially comprising Si, C, M and O, and/or
- ② an aggregate comprising crystalline ultrafine particles having a particle diameter of 500 Å or less essentially consisting of β -SiC, MC, a β -SiC-MC solid solution, and MC_{1-x} , and amorphous SiO_y and MO_z , wherein the Si-M-C-O substance comprises 5 ~ 70 % by weight of Si, 0.5 ~ 45 % by weight of M, 20 ~ 40 % by weight of C, and 0.01 ~ 30 % by weight of O (where M is at least one type of element selected from the group consisting of Ti, Zr, and Hf, and $0 < x < 1$, $0 < y < 2$ and $0 < z \leq 2$).

The fibers are obtained by the method for manufacturing fibers characterized by the following [four] steps:

In the first step, a polycyclic aromatic polymer containing silicon are obtained by allowing 1) and 2) below to undergo a reaction by heating and / or melting at a temperature within the range of 200 ~ 500 °C where

- 1) is a random copolymer in which at least part of silicon atoms of transition metal-containing organosilicon polymer comprising mainly the bond unit (S - CH₂), or the bond unit (Si - CH₂) and the bond unit (Si - Si), wherein side chains of Si atoms have a hydrogen atom, lower alkyl group, phenyl group, or a silyl group, and at least part of the main skeleton silicon atoms, which comprises the above-mentioned bond unit, are bonded to M (M is one type of element selected from the group consisting of titanium, zirconium, and hafnium) directly or via oxygen atoms, are bonded to carbons of aromatic rings of a polycyclic aromatic compound which is petroleum- or coal-pitch, or

- the compound resulting from its thermal treatment, and is obtained from the pitch containing organic solvent-insoluble matters; and
- 2) is a polycyclic aromatic compound in the mesophase or the dual phase of mesophase and optically isotropic phase obtained from petroleum- or coal-pitch.

In the second step, the spinning dope for the above-mentioned polycyclic aromatic polymer containing metals is prepared for spinning. In the third step, the spinning material yarn is made infusible under or in the absence of tension. And in the fourth step, said infusible spun fibers are sintered in vacuum or an inert gas ambience at a temperature within the range of 800 ~ 3000°C.

Note that the present applicant's application (2) filed on August 11, 1990, as well as the application (11) filed on September 1, 1989 are incorporated into the present specification by reference.

The continuous inorganic fiber bundle that is usable in the present invention is opened, thinly extended, pulled and arranged in one direction while tension is applied thereto.

Generally used matrix metals include Al, Ti, Cu, Ni, their alloys, and Fe-based heat resistant alloys, etc.

Generally used thermal spraying methods include gas spraying method, arc spraying method, plasma spraying method, etc.

The fibers that are pulled and arranged in one direction are thermal sprayed with matrix metal which is instantly melted by operating thermal spraying. A prepregated sheet, which is a sheet-type intermediate material, is thus obtained. The prepregated

sheet may have any thickness that is moldable, and it usually has a thickness of about 100 ~ 200 μm .

For the mold for setting a laminate of prepregnated sheets formed by laminating required pieces of the above-mentioned prepregnated sheets to allow the obtained FRM to maintain its fiber volume ratio and its shape constant, it is usually preferable to use metals or alloys which have a melting point higher than that of the matrix metal and also have the tendency to undergo plastic deformation. For example, when the matrix is of Al, the use of a mold made of Cu is preferable.

Mold 1 illustrated in Figure 1 is an example of the above-mentioned mold which has a preferable shape for use.

Preferably, the inside of the mold and the prepregnated sheet which is set into the mold have an identical shape. Also preferably, the inside of mold 1 has dimensions (vertical and horizontal lengths) larger than the dimensions (vertical and horizontal lengths) of the prepregnated sheet being set into the mold, namely up to 1.01 times as large as the dimensions (vertical and horizontal lengths) of the prepregnated sheet set in the mold. If dimensions (vertical and horizontal lengths) of the inside of mold 1 are excessively larger than the dimensions (vertical and horizontal lengths) of the prepregnated sheet, a gap is left between mold 1 and the prepregnated sheet, even though a laminate of prepregnated sheets 2 is set into mold 1. As a result, the melted matrix metal flows into the gap section during liquid phase diffusion bonding, preventing the mold from maintaining its fiber volume ratio constant.

Moreover, mold 1 is acceptable if the top and bottom surfaces thereof are as flat as those obtained from a normal molding die. If the bottom face of mold 1 is excessively

uneven, a gap is left between mold 1 and the bottom face of the mold. As a result, the melted matrix metal flows out of the mold into the gap section during liquid phase diffusion bonding, preventing FRM from maintaining its fiber volume ratio constant.

Figure 1 is a preferable example illustrating the state in which prepregnated sheet laminate 2 is set into mold 1.

The preferably usable material metal for a metal foil bag to seal the mold in which a laminate of prepregnated sheets is set has a melting point higher than that of the matrix metal. In the case in which the melting point of the material metal of the above-mentioned metal foil bag is no more than that of the matrix metal, the above-mentioned metal foil will break out due to melting, etc. and will not maintain its reduced pressure state during liquid phase diffusion bonding, which is not preferable. For example, when the matrix is of Al, stainless steel is preferably used for the material metal of the above-mentioned metal foil bag.

The preferable thickness for the metal foil bag is 10 ~ 100 μm . If the thickness is no more than the above-mentioned level, the metal foil bag will break out when the mold having a laminate of prepregnated sheets set therein is sealed, or the entire metal foil bag will melt when heat is applied to seal the bag.

[The metal foil bag] which is thicker than the above-mentioned level makes its manufacturing or processing difficult. Moreover, when the metal foil bag is vacuum vented, the thicker metal foil bag tends not to deform itself, leaving the gap between the bag and top and bottom faces of the mold. And during liquid phase diffusion molding, the melted metal flows into gap sections outside the mold through the gap to be lost from the mold. Hence, the objective of the present invention cannot be achieved.

The acceptable metal foil bag is large enough to accommodate the mold in which a laminate of prepregnated sheets is set. Preferable size of the bag is about the same as that of the mold in which a laminate of prepregnated sheet is set. A metal foil bag which is excessively larger than the mold is not only ineffective but also uneconomical.

Preferable methods for sealing the metal foil bag containing the mold in which a laminate of prepregnated sheets is set include the method in which the metal foil bag has a mold insertion edge and a vacuum vent edge, wherein the mold is first inserted into the metal foil bag from the insertion edge, and sealed at that insertion edge, and second, the metal foil bag is vacuum vented at the vacuum vent edge and sealed at that vacuum vent edge under reduced pressure.

As to the means for sealing the above-mentioned metal foil bag, preferably usable means to obtain the above-mentioned edges with excellent welding include a laser welding method, electron beam welding method, and TIG welding method.

According to the present invention, since the top and bottom faces of the mold can be sealed by the use of a metal foil, the melted metal does not leak from the mold during liquid phase diffusion bonding. Therefore, FRM can maintain its fiber volume ratio or shape constant.

The above-mentioned metal foil bag which is sealed under reduced pressure is subjected to liquid phase diffusion bonding by the use of an ordinary hot press machine.

Preferable conditions for the liquid phase diffusion bonding depend on the matrix metal of FRM. However, when the matrix is of Al, the preferable heating temperature is within the range of 660 ~ 700°C while the preferable hot press duration is within the range of 30 ~ 300 seconds.

(Effects of the Invention)

According to the present invention, the following excellent effects can be obtained:

- (1) The metal foil bag containing the mold in which a laminate of prepregnated sheets is set is thinner than a thin metal plate-made container; therefore, it can be manufactured or processed easily.
- (2) Since a laminate of prepregnated sheets is set in a mold and the mold is vacuum sealed in the above-mentioned bag, FRM that maintains its fiber volume ratio (V_f) and shape constant can be manufactured.

(Embodiment)

An embodiment is shown below.

Embodiment 1

A bundle of 400 Si - Ti - C - O fibers having a diameter of 10 μ m (Chirano® manufactured by Ube Industries, Ltd.) was opened uniformly, and the fibers were pulled and arranged in one direction under tension. Then, the fibers being pulled and arranged in the manner as described above were plasma sprayed with melted aluminum to form a prepregnated sheet. At that time, the nozzle of the plasma spray device was 140 mm apart from the fiber surface.

The prepregnated sheet thus obtained had a thickness of 130 ~ 150 μ m. Sheets having [a length of] 90 mm in the fiber direction and [a width of] 60 mm in the direction perpendicular to the fibers were cut out from the prepregnated sheet. Five of the sheets were laminated in one direction, and the laminate was set into the mold. A set of the laminate and the mold was inserted into a stainless foil bag (thickness: 60

μm) and the insertion edge thereof was welded by the use of laser beams. Then, the bag was vacuumed at the other edge until the pressure in the bag reached 1×10^{-2} mmHg. Then, the part was welded by the use of laser beams.

The above-mentioned metal foil bag, whose both edges were sealed under reduced pressure, was placed in a hot press machine and heated to 660 °C. Then, the molding die was pressed for one minute at a pressure of 100 kg / cm² by the use of a hydraulic press machine to obtain FRM. The obtained FRM had a uniform fiber distribution freed from the part containing only Al, and it was able to maintain its fiber volume ratio constant.

Additionally, the obtained FRM maintained a predetermined shape along the mold.

4. Brief Description of the Drawings

Figure 1 is a perspective view illustrating the mold in which a laminate of prepregnated sheets is set.

1: Mold 2: A laminate of prepregnated sheets

Patent Applicant: Ube Industries, Ltd.

Figure 1

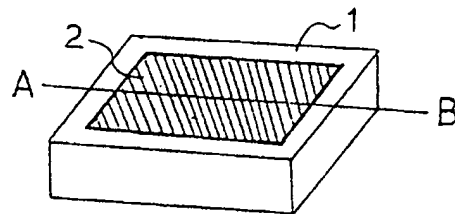
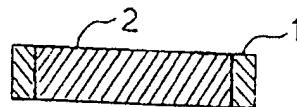


Figure 2



Written Amendment/Correction (Formality)

January 12, 1990

To: Commissioner of Patents

1. Case Identification

Patent Application H01-247954

2. Title of the Invention

Method for Manufacturing a Fiber Reinforced Metal Matrix Composite

3. Amended by:

Relationship with the Case: Patent Applicant

(020) Ube Industries, Ltd.

12-32, Nishi-Hommachi 1-chome, Ube, Yamaguchi-ken

Yasuo Shimizu, Representative (Seal impression)

4. Date of Invitation to Correct (Mailing Date)

December 26, 1989

5. Object of Amendment

Brief Description of the Drawings

6. Contents of Amendment

Page 17, line 7 of the specification

Insert the following sentence after "...a perspective view illustrating the mold."

"Figure 2 is the vertical cross-sectional view of the mold along the A-B line as shown in Figure 1."

(Stamped by Application Department (JPO) on January 12, 1990).